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Method and ink sets for marking and authenticating articles

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Method and ink sets for marking and authenticating articles

The invention is about security documents and articles, i.e. bank notes, value papers, identity documents, cards, tickets, labels, security foils, security threads and the like, which can be easily authenticated by stationary or portable electronic equipment, such as currency acceptors, processing machines, ticket validators, hand-held authentication devices, etc., and of methods to produce and authenticate such security documents or articles through the application of dyes or pigments exhibiting a specific spectral absorption.

The increasing availability to the general public of desk-top color printing and reproduction equipment, such as color computer printers, color scanners and color copiers, has raised an additional threat to document security. In particular, the currently used security features do not provide sufficient protection against counterfeits at automatic banknote acceptors, where exclusively electronic means are used for the authentication.

Known security features suitable for authentication with electronic means are described for example, in EP-B-0 053 124 and EP-B-0 053 183, EP-B-0 053 125, EP-B-0 024 053, EP-B-0 340 898, or EP-B-0 537 431. These features are based on luminescence, magnetic properties, or on absorption in the non-visible range of the electromagnetic spectrum. However, the exploitation of several of said physical effects is accompanied with drawbacks. For example, in the case of luminescence, the to-be-measured light intensities are generally low, requiring sophisticated technology, including the shielding of ambient light and of other potentially perturbing effects. Magnetic properties are less suited as a security feature, because they require in gen-

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eral a mechanical contact between the bank note and the magnetic sensor device (reading head). This constitutes a major source of errors, caused by jamming of 'in-bad-shape' bank notes in the reader device.

A shortcoming of the 'classic' UV or IR-absorber based banknote security features, such as disclosed in EP-A-0 024 053, is noteworthy that they rely on the use of a single absorber compound as a covert security element outside the visible range of the spectrum. The presence of the covert security element can be revealed with the help of commonly accessible, cheap CCD cameras (e.g. door-watcher cameras, having a sensitivity range of 300 to 1100 nm wavelength) and commonly accessible generic UV and IR filters, available in photo-shops. Generic UV- and IR-absorbing compounds are furthermore used in many areas of current technology, noteworthy in certain electrophotography toners, and are thus commercially available as well.

It was therefore the object of the present invention to provide a protection for a security article against counterfeiting, which overcomes the above described drawbacks of the prior art and which allows an easy authentication of said article by machines, such as currency acceptors, ticket validators, etc..

The above problem is solved in particular by a printing ink and/or a set of printing inks and the use thereof for marking and/or authenticating an article, as defined in the independent claims.

The present invention relies on the selection of dyes or pigments which cannot be perceived correctly by the human eye, in particular on a selection of a set of such dyes or pigments con-

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stituting a color space which in its entirety cannot be perceived by the human eye.

The human eye's color perception is based on the signals of only three different types of receptors, one for long wave (600 nm; red), one for intermediate wave (550 nm; green), and one for short wave (450 nm; blue) light. In addition to these, a general white light receptor, having a sensitivity maximum at about 550 nm, is present, too. The relative sensitivity curves of the three photoreceptors, which correspond to the spectral absorption curves of the related photopigments in the eye, have been experimentally determined and are known as the "Color Matching Functions", as defined by the *Commission Internationale d'Eclairage* (C.I.E.). They are the basis of all human color reproduction technology. Every visible color can noteworthy be expressed within this CIEXYZ-system by three basic color coordinates: X (red), Y (green) and Z (blue); confining the human color vision to a three-dimensional color space. The human eye noteworthy lacks light perception in the ultraviolet (UV, below 400 nm wavelength), and in the infrared (IR, above 700 nm wavelength) range of the electromagnetic spectrum.

Huge efforts and work have been dedicated in the past to the development and the selection of dyes, pigments and other devices, in order to reproduce colors as "truly" as possible, as set forth by the properties of the human eye. Today's color reproduction technology relies in fact on a narrow selection of particularly adapted printing pigments, of carefully selected cathode ray tube phosphors and of sophisticated optical filters for color cameras and scanning elements.

Color in security applications, however, has a totally different purpose. Objects need not have to be depicted in "true" color,

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but quite often, color has a mere functional sense, e.g. to distinguish between the different denominations within a currency series.

To counteract the modern threat of generally available and ever more sophisticated color reproduction equipment to currency, value documents and other articles whose reproduction is undesirable, the present invention discloses a novel method of marking and/or authentication, based on the use of selected dyes or pigments. The present invention is based on a deliberate departure from the base colors of the three-dimensional CIEXYZ color space. The marking on a value document or article according to the present invention comprises i) visible colors which are not used in ordinary color reproduction or printing, ii) narrow-band absorbers which do only yield pastel shade color, and iii) invisible 'colors' which correspond to absorption outside the visible range (400 to 700 nm) of the electromagnetic spectrum, either in the ultraviolet (below 400 nm) or in the infrared region (above 700 nm).

Thus, the present invention is related to a printing ink, comprising at least one dye or pigment having at least one absorption maximum in the visible range of the electromagnetic spectrum which is substantially different from the absorption maxima of the base colors of the CIEXYZ system, or which is outside the visible range of the spectrum, and/or having an absorption band in the visible range of the electromagnetic spectrum whose band width at half intensity is narrower than 2400 cm^{-1} , preferably narrower than 2000 cm^{-1} , and most preferably narrower than 1500 cm^{-1} .

Furthermore, the present invention is related to set of printing inks, comprising at least two printing inks as defined above.

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In particular, the present invention discloses the use of a 'hyperchromic color system', embodied by a corresponding set of dyes or pigments and/or a corresponding ink set, and comprising at least 3, preferably at least 4 base colors which are chosen such as to have at least one absorption maximum which is substantially different from the absorption maxima of the base colors of the CIEXYZ-system (which comprises the additive base colors red, green, blue; or the subtractive base colors yellow, magenta and cyan, respectively). The color system according to the present invention may hereby comprise selective UV, visible and IR absorbing components, embodied by corresponding dyes or pigments. It may also comprise selective UV, visible and IR reflecting components, embodied by corresponding pigments. Preferably, the visible dyes or pigments are chosen to have spectral transmission or reflection maxima which are different from the 'CIEXYZ-maxima' located at 450 nm (blue), 550 nm (green) and 600 nm (red). Preferably, the color system according to the invention comprises at least one dye or pigment absorbing in the UV or in the IR region of the electromagnetic spectrum; more preferably, the color system comprises at least two dyes or pigments absorbing in the IR region of the electromagnetic spectrum.

Of particular interest in the context of the present invention are narrow-band absorbing dyes or pigments, as they allow for the introduction of more spectral variety inside a given, available spectral range (such as the 300 nm to 1100 nm range). Within the visible spectral range, preferred dyes or pigments have substantially narrower absorption bands than those of the eye's CIEXYZ Color Matching Functions. It is then possible to cover even the visible spectral domain with more than three of

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said dyes or pigments, hereby creating a hyperchromic visible color space.

The eye's color matching functions have noteworthy the following properties:

	maximum of sensitivity	bandwidth at half intensity
blue absorber:	445 nm (22'500 cm^{-1})	55 nm (2'800 cm^{-1})
green absorber:	555 nm (18'000 cm^{-1})	110 nm (3'600 cm^{-1})
red absorber:	595 nm (16'800 cm^{-1})	85 nm (2'400 cm^{-1})

The first of the indicated numbers refers to the wavelength (in nm); the second number to the energy (in cm^{-1}), respectively.

Conversion to 1000 cm^{-1} : $10'000/\text{wl}$

Bandwidth in 1000 cm^{-1} : $10'000 \cdot \text{bw}/\text{wl}^2$

(wl = wavelength in nm; bw = bandwidth in nm)

Substantially narrower absorption bands than the said color matching functions shall mean, in the context of the present invention, an absorption band having a band width at half intensity which is narrower than $2'400 \text{ cm}^{-1}$. In particular, the dye or pigment according to the present invention has preferably a band width which is lower than $2'000 \text{ cm}^{-1}$, more preferably a band width lower than $1'500 \text{ cm}^{-1}$. The band width of said dye or pigment should, however, be larger than 100 cm^{-1} , excluding rare-earth based extremely-narrow-band absorbers.

Narrow-band absorbing dyes or pigments are also of interest in the ultraviolet (300 - 400 nm) and in the infrared, in particular in the 700 nm to 1'100 nm wavelength range, which are detectable by the commercially available silicon photodetector devices, such as photodiodes, CMOS- and CCD-cameras. Using a couple of narrow band absorbing compounds in the said IR wavelength

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range allows noteworthy to implement graphic 'multicolor' security designs, comprising one or more invisible 'infrared colors'. In a particular embodiment, three IR-pigments, absorbing in the 700 to 800 nm, the 800 to 900 nm, and the 900 to 1'000 nm range, respectively, may be used to print a trichromatic picture in the infrared region of the electromagnetic spectrum, which is invisible to the unaided human eye. The picture can be camouflaged by overprinting it with one or more IR-transparent visible colors. The resulting trichromatic IR-picture may then be visualized or inspected with the help of a corresponding electronic 'IR-color' camera and a visual color display.

The dyes or pigments to be used according to the present invention may in general be selected among the organic molecular compounds, the organic polymeric compounds or the inorganic compounds. As a general principle in the context of the present invention, a 'color' of the hyperchromic color system is embodied by a corresponding, single chemical compound, which may have one or several absorption bands in the 300 to 1'100 nm spectral region. A hyperchromic color system comprising at least 3, preferably at least 4 base colors is thus embodied by an ink or a set of inks comprising at least 3, preferably at least 4 different chromophoric compounds, i.e. such which have absorption spectra which are substantially different from each other in the 300 to 1'100 nm wavelength range. Substantially different means according to the present invention that the statistical correlation of two spectra represented by two vectors s_1 and s_2 , as expressed by the normalized scalar product $(s_1 * s_2) / (|s_1| * |s_2|)$, shall not exceed 0.95. The vectors s_1 and s_2 are explained below.

The dyes or pigments according to the present invention need thus not to be all very different in color; the hyperchromic color system could, e.g., comprise two different yellow, two

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different blue, and two different red dyes or pigments in varying proportions. A photocopying machine would have to reproduce these colors using a single yellow, a single blue and a single red dye. A corresponding detection device would rely, in contrary, on two different yellow, two different blue, and two different red channels, and thus be able to differentiate easily between the original and the copy.

Dyes and pigments which are useful for implementing the method and for making a printing ink or coating composition according to the present invention can be found in several substance classes. In a preferred embodiment they are selected from the group comprising cyanines (polymethines) and the related cyanin-type chromophores; quinones and the related quinone-type chromophores; porphines, phthalocyanines and the related macrocyclic chromophores; as well as heterosubstituted polycyclic hydrocarbon chromophores. A chromophore, in the context of the present invention, is a "color-generating" chemical group, exhibiting absorption somewhere in the 300 nm to 2'500 nm, wavelength range. The chromophore may have a molecular or a polymeric structure; it may furthermore carry chemical substituents of all kind, and/or be linked into or grafted onto a polymer chain.

Cyanine (polymethine) dyes are known in the art and used as photographic sensitizers (D.M. Sturmer, *The Chemistry of Heterocyclic Compounds*, Vol 30, John Wiley, New York, 1977, pp 441-587; Eastman Kodak). In a more recent application, stable representatives of this compound class, selected from the coumarins and rhodamines, were also used as laser dyes (J.B. Marling, J.H. Hawley, E.M. Liston, W.B. Grant, *Applied Optics*, 13(10), 2317 (1974)).

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Porphines and related molecules can be viewed as macrocyclic cyanine structures, conformationally rigidized by their cyclic nature, in particular in the presence of a coordinated metal ion, such as Mg^{2+} and other. As a consequence, their long-wave absorption band is very sharp and they are almost ideal examples of a narrow-band absorbing dye according to the invention. Chlorophyll-a (absorption band at 660 nm; extinction coefficient ϵ of 85'000) is a dye of this class (K. Sauer et al., J. Am. Chem. Soc. 88, (1966), 2681-88). As porphines and related molecules are rather difficult to synthesize, their industrial use is restricted to the naturally available compounds.

Phthalocyanines and related molecules are the "industrial variant" of porphines. They generally absorb at the long wavelength end of the visible spectrum, and the largeness of their absorption band depends heavily upon their crystal packing (aggregation). Narrow-band absorption is generally observed in diluted solution of such dyes, and for certain pigments in the solid state, in particular if a stacking of the pigment's chromophoric groups is absent. The class of phthalocyanines at large comprises as well the higher-conjugated analogs, such as the naphthalocyanines, which absorb farther in the IR, as well as the heterosubstituted analogs of phthalocyanines; the common point defining this compound class is that all of its members are derived from aromatic ortho-dicarboxylic acids or from their derivatives.

Quinone dyes are known in the art and used for textile and related dyeing applications (e.g. indigoid dyes, anthraquinone dyes, etc.). Electronegative groups or atoms along the quinone skeleton can be present to enhance the intensity of the absorption band, or to shift it to longer wavelengths. Some dyes of this class, especially those which carry no NH or OH groups,

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show narrow absorption bands. Examples of such dyes are thioindigos, N,N'-dialkylindigos, N,N'-alkylene-indigos, etc.

Heterosubstituted polycyclic hydrocarbon dyes are rigid, planar molecular structures, at the image of the graphite lattice, carrying appropriate substituents. Peryleneimides, quinacridones, dioxazines, etc. are examples of such dyes.

An important aspect in prospecting for narrow-band absorbing pigments is to avoid aggregation between the individual dyestuff molecules; a tendency which is inherent to most organic polycyclic compounds and even more enhanced in the case of a molecule's capability to undergo hydrogen bonding. Aggregation in most cases broadens the spectral absorption bands; it is thus to be considered an undesired feature in the context of the present invention. There are different ways to solve this problem:

- Use of dye molecules which do not form said absorption-band-enlarging aggregates.
- Use of dye molecules which are soluble in an inert polymeric carrier compound; the correspondingly obtained mass-stained and comminuted polymer may be used as a printing pigment.
- Use of dye molecules which are co-polymerizable into an established polymer matrix, e.g. polystyrene, or which are graft-able onto an existing polymer; the correspondingly obtained mass-stained and comminuted polymer may be used as a printing pigment or as a varnish additive.

A large number of suitable pigments and dyes for embodying the invention have already been described in the literature. However, ordinary commercially available colorants are purposely designed to fit the human eye's broad-line color matching functions. Most of the known narrow line absorbing molecules or compositions are, for this reason, not industrially exploited as

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pigments or dyes, due either to their "lack of color strength" as perceived by the human eye, or to their light dependent color change ("untrue colors"). The same holds as well for the commercial infrared absorbing dyes or pigments, which were designed for use in optical recording materials, where a rather broad absorption band is required.

The absence of a commercial market for most of the dyes or pigments which are useful in the context of the present invention increases the security potential of the disclosed method and of its embodiments. The application of non-commercial dyes and pigments in the field of security printing requires their dedicated production and enables in consequence an effective control of the source of the material; a very crucial requirement to war-rant security.

Preferred dyes according to the present invention are shown in Fig. 2. Fig. 2a is a Hexadeca-(3-ethoxy-1-thiophenolato)-phthalocyanato-zinc(II) absorbing in the region of 780 nm. Fig. 2b is a Deca-(3-ethoxy-1-thiophenolato)-hexa-(3-methyl-1-thiophenolato)-phthalocyanato-zinc(II) absorbing in the region of 850 nm. The formula of Fig. 2b is for an industrial product and represents a statistical mean over a certain distribution of the substituents.

In a hyperchromic color system, the choice of the base colors is free, under the condition that said base colors have substantially different absorption spectra, such as defined above. The correlation between a measured absorption spectrum $S(\lambda)$ and the corresponding 'hyper-color coordinates' $x_1, x_2, x_3, x_4, \dots$ in the chosen hyperchromic color system, which indicate the concentrations or 'optical densities' of the individual chromophoric compounds, can be established with the help of linear algebra. De-

iving 'hyper-color coordinates' allows noteworthy to assign a statistically independent value to each dye or pigment of the hyperchromic color system, if the dyes or pigments of the set have partially overlapping absorption spectra. The method shall be outlined in the following, using commonly known formalism of matrix algebra.

According to the method, an standard absorption spectrum $S(\lambda)$ of a dye or pigment is expressed by a vector $s = (s_1, s_2, s_3, \dots, s_n)$, wherein $s_1, s_2, s_3, \dots, s_n$ are the measured spectral absorbance values (optical densities $OD = \log(I_0/I_{\text{reflected}})$, as defined in the art) at n different wavelengths $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$. Said wavelengths can hereby be chosen freely, but they should be related to the dyes or pigments used, and noteworthy allow a discrimination of the different constituents of the hyperchromic color system.

The hyperchromic system shall further comprise m different colorants; there are thus m of the said vectors s , representing the dyes' or pigments' absorption spectra. Said m vectors s are arranged in a rectangular matrix A , comprising m columns of n elements each. Any linear combination of colorants within the chosen hyperchromic color system will result in an absorption spectrum $y = (y_1, y_2, y_3, \dots, y_n)$, which can be expressed through the matrix equation:

$$A * x = y$$

wherein A is the said matrix of dimensions $(n \times m)$; x is the vector of the m linear factors, corresponding to the hyper-color coordinates, and y is the vector of the resulting n spectral absorption values.

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On the other hand, knowing the matrix A, a measured absorption spectrum y1 can be expressed in terms of hyper-color coordinates x, using the classic 'least-squares' formula of linear algebra:

$$x = (A' * A)^{-1} * A' * y1$$

wherein A' denotes the transposed of matrix A, and $(A' * A)^{-1}$ denotes an inverse matrix. The goodness of fit of the approximation can be assessed by statistical criteria, such as the sum of deviations squared $(y - y1)' * (y - y1)$, or others known in the art. Such criteria may serve as a further authentication tool.

Other, similar algorithms of linear algebra may be used as well to the same purpose, noteworthy the algorithm of Singular-Value-Decomposition (SVD), which is related to the problem of equation-solving and the method of 'least-squares'.

The above stated means that there exists a $(m \times n)$ matrix M, which relates the measured spectrum y to the 'hyper-color coordinates' x of the corresponding color-space through a simple mathematical transformation:

$$x = M * y$$

Said matrix M $= (A' * A)^{-1} * A'$ can be calculated from the absorption spectra of the base colors of the hyperchromic color system.

The above described dyes or pigments of the hyperchromic color system, incorporated into a printing ink or coating composition, or into a set of printing inks or coating compositions, are used according to the present invention in a method for marking an article, such as a banknote, a document, a ticket, a foil, a

thread, a label, a card, or a commercial good, comprising the step of providing on said article a marking, e.g. in the form of indicia or a user-defined design, which is applied by using at least one printing ink or coating composition, or a set of printing inks or coating compositions as defined above.

Furthermore, the above described dyes or pigments, implemented in a printing ink or coating composition, or in a set of printing inks or coating compositions, and applied to an article, are used according to the present invention in a method for authenticating said article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good, comprising the steps of:

- a) measuring an optical absorbance, reflectance or transmittance spectrum of said article marked by the method described above, in the UV, and/or visible and/or IR wavelength domain of the electromagnetic spectrum;
- b) comparing the spectrum and/or information derived therefrom with a corresponding spectrum of an authentic item and/or information derived therefrom.

The marking and the authenticating part of the method may be performed together or separate from each other, by a same or a different operator, at the same or at a different location, using either a same or a different device.

Inks and coating compositions useful to impart the marking may be chosen from the group of pasty inks, such as intaglio, letterpress and offset inks; from the group of liquid inks, such as screen-printing, helio-flexo, and gravure inks; or from the group of drop-on-demand and of continuous ink-jet inks. Useful coating compositions to impart the marking comprise furthermore

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toners for electrostatic (dry) or electrophoretic (wet) photo-printing processes.

The application of said user-defined marking design is performed with the help of inks or ink sets comprising an ink for each of the selected base-colors of the extended, hyperchromic color space. An individual ink may also comprise more than one dyes or pigments embodying said base-colors.

The spectra of the printed design may be measured as known in the art, using either: a combination of a broad-band emitting light source and a plurality of narrow-band sensitive photodetectors; a combination of a broad-band sensitive photodetector and a plurality of narrow-band emitting light sources; or a combination of a broad-band emitting light source and a dispersive or diffractive spectrometer device. A combination of a plurality of narrow-band emitting light sources, such as LEDs, and a broad-band sensitive imaging device, such as a CCD- or CMOS-camera, may furthermore be used to perform a spectral or hyperspectral imaging of the printed design.

The step of deriving and comparing hyper-color coordinates, rather than crude spectral absorbance, reflectance or transmittance values, brings in the advantage of robustness. A hyperchromic color space can noteworthy be chosen to contain first pigments for decorative purposes, together with second pigments for security purposes, wherein the decorative and the security pigments have partially overlapping absorption spectra. It would be difficult, in such a case, to identify the presence and the amount of a security pigment in a marking without transforming the spectral information to the statistically independent quantities of the hyper-color coordinates.

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The method of document protection according to the present invention and the resulting security documents or articles are highly suited for the authentication by machines, such as used in automatic currency acceptors, teller machines, high-speed sorting machines, ticket validators and the like. Authentication by machines is noteworthy limited to the checking of such security features whose detection is intrinsically rapid and which do not require a close contact between the document and the reading device, due to the danger of obstruction (jamming). Optical methods are therefore among the preferred ones for machine-authentication. Due to the use of selective absorption rather than emission, the available light, as reflected from the document, is more than sufficient, allowing for a very rapid measurement cycle, and thus for a high-speed operation of the authentication device.

The invention will now be further explained with the help of the Figures as well as examples. These figures and examples are not intended to limit the scope of the present invention.

Fig. 1: shows a schematic embodiment of an extended color space according to the present invention, illustrating the use of narrow-band absorbing pigments or dyes inside and outside the visible range of the spectrum;

Fig. 2: shows the formulas of two IR-absorbing compounds which are useful in the context of the present invention.

Fig. 3: shows the spectral reflectance characteristics of a feature printed with the ink of example 1

Fig. 4: shows the spectral reflectance characteristics of a feature printed with the ink of example 2

Fig. 5: shows the spectral reflectance characteristics of a feature printed with the ink of example 3

Fig. 6: shows the spectral reflectance characteristics of a feature printed with the ink of example 4

In a first, schematic example as shown in Fig. 1, an extended hyperchromic color space is constituted by ten narrow-band absorbing dyes or pigments labeled 1 to 10. They have absorption maxima within the spectral range of 300 to 1'100 nm wavelength. Dye 1 has an absorption maximum in the UV (350 nm). Dyes 2, 3, 4, 5 have absorption maxima in the visible (425, 500, 575, 650 nm), and dyes 6, 7, 8, 9, 10 have absorption maxima in the IR (725, 800, 875, 950 and 1'025 nm wavelength). In particular, the visible range is covered by four dyes, instead of three corresponding to the human eye's receptors. Visible dyes 3 and 4 are noteworthy selected as to have an absorption maximum of 500 nm, falling in between the blue (450 nm) and the green (550 nm), respectively of 575 nm, falling in between the green (550 nm) and the red (600 nm) photoreceptor of the human eye. Colors such as these, if combined with a pure blue (425 nm) and a pure red (650 nm) dye, will result impossible to reproduce by the standard trichromy process colors, because four constraints cannot be accommodated by three variables.

An article is now marked using an ink or an ink set comprising one or more of said narrow-band absorbing dyes or pigments. The color information comprised on said article is hereby effectively chosen out of a ten-dimensional manifold, although humans only can see and describe it in terms of a three-dimensional color perception. The human eye's impression of the security article's color corresponds thus to a projection of said article's

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real color information onto a three-dimensional color perceiving system. This projection is performed under the light of the illuminating source used to view the document. Changing the light quality of said illuminating source may lead to a different projection, and therefore to a different color perception. The use of visible narrow-band absorbing dyes or pigments in coatings invariably results in an illumination-dependent variation of the shades ("untrue" colors).

When said article, e.g. a banknote or a document, is reproduced by a color copier, or scanned by a color scanner, its spectral information in the visible domain is channeled by corresponding optical filters into the three base colors red, green and blue. A projection of the extended color information contained on said document onto these three color channels is performed under the particular light of the copier or scanner. When the scanned color information is subsequently reproduced by printing, standard dyes or pigments, corresponding to the human eye's three-dimensional color perception, are deposited on the paper, in place of the original, narrow band absorbing colorants. The resulting reproduction will look about the same, if seen under the same light which was used to scan the original. However, it may look quite different if seen under a different light than that used to scan the original.

In particular, the optical features outside the visible range, i.e. the ones located in the UV (UV-dye 1) and the ones located in the IR (IR-dyes 6 to 10), are not reproduced by common reproduction equipment, and are thus lacking on the copy. The visible features, due to dyes 2 to 5, will be reproduced, but not correctly. The resulting "color difference" between the original and its counterfeit can be evidenced to the human eye by comparing both under at least two different visible light sources,

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and, in the complete UV to IR range of the spectrum, by photodetectors or spectroscopic means.

In the following the preparation and use of ink sets according to the present invention is illustrated at the examples of three different types of ink formulations:

Formulation 1 :

Intaglio printing ink set formulation with 5 inks

Addition product of tung oil and maleic acid modified phenolic resin in a high boiling mineral oil (PKWF 28/31)	35%
Long oil alkyd resin	7.5%
Alkylphenolic resin modified with raw tung oil in ink solvent 27/29 (Shell Industrial Chemicals)	16%
Polyethylene wax	1.5%
Calcium carbonate	30.3%
Dyes and Pigments	4.5%
Ink solvent 27/29 (Shell Industrial Chemicals)	5%
Cobalt octoate (11 % metal)	0.1%
Manganese octoate (10 % metal)	0.1%

Dyes and pigments:

Ink 1: absorption peak at 470 nm

Acridine Orange Base (Aldrich)	1.0%
Calcium carbonate	3.5%

Ink 2: absorption peak at 850 nm

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Deca-(3-ethoxy-1-thiophenolato)-hexa-(3-methyl-1-thiophenolato)-phthalocyanato-zinc(II) (Avecia).	4.0%
Calcium carbonate	0.5%

Ink 3: absorption peak at 380 nm

Tinuvin 1130 (Ciba)	4.5%
Calcium carbonate	-

Ink 4: absorption peak at 980 nm

Long-wave NIR absorber (Avecia)	3.0%
Calcium carbonate	1.5%

Ink 5: absorption peaks at 620 and 780 nm

X-form copper phthalocyanine pigment	1.8%
Calcium carbonate	2.7%

The ingredients were mixed together and the mixture was homogenized by 2 passes on a triple-roll mill.

Formulation 2 :

Dry offset UV-drying ink set formulation with 3 inks

Epoxyacrylate oligomer	39%
Trimethylolpropanetriacrylate monomer	31%
Genorad 16 (Rahn)	1%
Talc	2%
Dyes and pigments	4.5%
Calcium carbonate	10.5%
Aerosil 200 (Degussa-Huels)	4%
Irgacure 500 (CIBA)	6%

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Genocure EPD (Rahn)	2%
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Dyes and Pigments:

Ink 1: absorption peak at 550 nm

Rhodamine B. (Aldrich)	1.5%
Calcium carbonate	3.0%

Ink 2: absorption peak at 780 nm

Octabutoxy copper(II) naphthalocyanine	4.5%
Calcium carbonate	-

Ink 3: absorption peak at 890 nm

Hexadeca-(3-ethoxy-1-thiophenolato)-phthalocyanato-zinc(II) (Avecia)	2.7%
Calcium carbonate	1.8%

The ingredients were mixed together and the mixture was homogenized by 2 passes on a triple-roll mill.

Formulation 3:

Gravure ink set formulation with 4 inks

Ethanol	32%
Ethyl acetate	45.3%
Dicyclohexylphthalate (Unimoll 66, supplied by Bayer)	4.5%
Fumaric acid modified rosin (Rokramar 7200, supplied by Robert Kraemer GmbH&Co)	3%
Polyvinylbutyral resin (Pioloform BN18, supplied by	12%

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Wacker-Chemie)	
Dyes and pigments	3.2%

Dyes and pigments:**Ink 1: absorption peak at 550 nm**

Rhodamine B base (Aldrich)	0.4%
Ethyl acetate	2.8%

Ink 2: absorption peaks at 610 and 680 nm

Luxol fast blue MSN (Aldrich)	3.2%
Ethyl acetate	-

Ink 3: absorption peak at 440 nm

Macroflex Yellow 6G (Bayer)	1.0%
Ethyl acetate	2.2%

Ink 4: absorption peak at 800 nm

Absorber dye IR P303 (Honeywell)	1.0%
Ethyl acetate	2.2%

The resins were dispersed with the solvents during 15 minutes using a laboratory dispersing equipment. The dyes were added subsequently and the formulation was further dispersed during 15 minutes. The viscosity of the resulting formulation was adjusted with a blend of ethyl acetate / ethanol 1:1 to reach the required printing viscosity (15-25" cup DIN4, depending on the application).

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To illustrate the reflection characteristics which are obtainable using the ink sets according to the given formulation embodiments, four printed samples were prepared:

Example 1: Intaglio ink, obtained by mixing Ink 1 and Ink 2 of formulation 1 (above) in a ratio 1:1 and printing on paper at 8 g/m². The reflectance spectrum is given in Fig. 3.

Example 2: Intaglio ink, obtained by mixing Ink 3, Ink 4 and Ink 5 of formulation 1 (above) in a ratio 1:1:1 and printing on paper at 8 g/m². The reflectance spectrum is given in Fig. 4.

Example 3: Dry-offset UV-ink, obtained by mixing Ink 1, Ink 2 and Ink 3 of formulation 2 (above) in a ratio 1:1:1 and printing on paper at 1 g/m². The reflectance spectrum is given in Fig. 5.

Example 4: Gravure ink, obtained by mixing Ink 1, Ink 2, Ink 3 and Ink 4 of formulation 3 (above) in a ratio 1:1:1:1 and applying on paper with a hand coater at 4 µm (theoretical wet film). The reflectance spectrum is given in Fig. 6.

The method of deriving 'hyper-color coordinates' is now further illustrated with the help of a schematic worked example which is shown in table 1 below. A reader device has 12 spectral channels centered at 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, and 950 nm wavelength, respectively. A different number of channels, at different values of wavelength, may be chosen as well. The channels need not even to be regularly spaced.

A hyperchromic color space comprising 6 base colors, is embodied by dyes or pigments having 6 substantially different absorption spectra. These dyes or pigments yield the 'optical density' responses 'Spec 1', 'Spec 2', 'Spec 3', 'Spec 4', 'Spec 5', and 'Spec 6', respectively, with the said reader device; the ensem-

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ble of these values constitute the matrix A defining the mathematical basis of the hyperchromic color space.

A measured unknown spectrum, 'Spec y', can be expressed in terms of hyper-color coordinates x of the hyperchromic color space by taking the product $x = (A' * A)^{-1} * A' * y$. In the worked example, the resulting color coordinates (CCRD) of y in terms of the 6 base colors are: 0.35, 0.10, 0.00, 0.40, 0.00, 0.15. This is exactly the linear combination which was used to construct y in this schematic worked example.

This example further illustrates the different matrices of the algorithm, in particular the matrix $M = (A' * A)^{-1} * A'$, which is used to transform a measured spectrum y into color coordinates x according to the formula $x = M * y$. For a given base color system and a given type of reader device, the matrix M must be calculated only once, and can then be stored in the reader device; as a part of the authentication algorithm. It can be interpreted as a sort of key which enables to extract the relevant color-coordinates out of a more abundant spectral information.

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Table 1: Schematic worked example of a determination of hyper-color coordinates

Input spectra (A):

	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5	Spec 6
400nm	0.200	0.000	0.000	1.200	2.000	0.050
450nm	1.000	0.050	0.000	1.000	1.800	0.100
500nm	0.200	0.300	0.050	0.500	1.500	0.200
550nm	0.050	1.200	0.200	0.200	1.000	0.500
600nm	0.000	0.200	0.500	0.050	0.500	0.100
650nm	0.000	0.050	1.500	0.050	0.100	0.000
700nm	0.000	0.000	0.500	0.200	0.000	0.000
750nm	0.000	0.000	0.200	1.000	0.050	0.000
800nm	0.000	0.000	0.050	0.300	0.200	0.000
850nm	0.000	0.000	0.000	0.050	0.900	0.050
900nm	0.000	0.000	0.000	0.000	0.200	0.200
950nm	0.000	0.000	0.000	0.000	0.100	1.100

Measured spectrum (y):

	Spec y
400nm	0.560
450nm	0.770
500nm	0.330
550nm	0.300
600nm	0.060
650nm	0.030
700nm	0.080
750nm	0.400
800nm	0.120
850nm	0.030
900nm	0.030
950nm	0.170

Matrix $A'A$:

	1	2	3	4	5	6
1	1.083	0.170	0.020	1.350	2.550	0.175
2	0.170	1.575	0.430	0.453	1.845	0.685
3	0.020	0.430	2.835	0.480	0.695	0.160
4	1.350	0.453	0.480	3.868	5.335	0.368
5	2.550	1.845	0.695	5.335	11.652	1.325
6	0.175	0.685	0.160	0.368	1.325	1.565

Matrix $(A'A)^{-1}$:

	1	2	3	4	5	6
1	2.134	0.297	0.077	-0.194	-0.434	0.037
2	0.297	1.028	-0.108	0.210	-0.286	-0.280
3	0.077	-0.108	0.378	-0.081	0.014	0.007
4	-0.194	0.210	-0.081	0.803	-0.360	0.054
5	-0.434	-0.286	0.014	-0.360	0.399	-0.081
6	0.037	-0.280	0.007	0.054	-0.081	0.813

Vector $A'y$:

123456

0.9630.5110.2782.1253.4280.521

Vector $x = (A'A)^{-1}A'y$:

123456

CCRD 0.3470.1030.0030.3990.0010.154

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Matrix $(A^*A)^{-1}A^*$:

	S1	S2	S3	S4	S5	S6
400nm	-0.672	-0.274	-0.054	0.208	0.276	-0.050
450nm	1.177	0.016	0.016	-0.023	-0.098	0.012
500nm	-0.221	-0.017	-0.016	-0.107	0.231	-0.009
550nm	0.024	0.844	-0.049	0.054	-0.075	0.004
600nm	-0.125	-0.009	0.171	-0.133	0.123	-0.009
650nm	0.077	-0.128	0.560	-0.107	0.029	-0.009
700nm	-0.000	-0.012	0.173	0.120	-0.065	0.014
750nm	-0.201	0.175	-0.005	0.769	-0.337	0.051
800nm	-0.141	0.001	-0.003	0.165	-0.027	0.000
850nm	-0.398	-0.261	0.009	-0.281	0.337	-0.030
900nm	-0.079	-0.113	0.004	-0.061	0.064	0.146
950nm	-0.003	-0.336	0.009	0.023	-0.049	0.886

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Claims:

1. Printing ink, comprising at least one dye or pigment having at least one absorption maximum in the visible range of the electromagnetic spectrum which is substantially different from the absorption maxima of the base colors of the CIEXYZ system and/or having an absorption band in the visible range of the electromagnetic spectrum whose band width at half intensity is narrower than 2400 cm^{-1} , preferably narrower than 2000 cm^{-1} , and most preferably narrower than 1500 cm^{-1} .
2. Printing ink according to claim 1, further comprising at least one other dye or pigment having at least one absorption maximum in the ultraviolet or in the infrared region, preferably in the near-infrared region of the electromagnetic spectrum.
3. Printing ink according to any one of claims 1 or 2, comprising at least three, preferably at least four different dyes or pigments having absorption spectra which are substantially different from each other.
4. Printing ink according to any one of claims 1 to 3, comprising at least two, preferably at least three different dyes or pigments having at least one absorption maximum in the infrared range, preferably the near-infrared range of the electromagnetic spectrum.
5. Printing ink according to any one of claims 1 to 4, comprising at least four different dyes or pigments having at least one absorption maximum in the visible range of the electromagnetic spectrum.

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6. Printing ink according to any one of claims 1 to 5, further comprising a reflecting pigment.
7. Set of printing inks, comprising at least two printing inks according to any one of claims 1 to 6.
8. Set of printing inks according to claim 7, comprising at least three, preferably at least four different printing inks according to any one of claims 1 to 5 each having a dye or pigment which is different from the dyes or pigments in the other printing inks.
9. Set of printing inks according to claim 8, wherein the different dyes or pigments have at least one absorption maximum in the visible range of the electromagnetic spectrum.
10. Set of printing inks according to any one of claims 6 to 9, wherein at least one printing ink, preferably at least two and, more preferably at least three printing inks comprise a dye or pigment having at least one absorption maximum in the ultra-violet or in the infrared region, preferably in the near-infrared region of the electromagnetic spectrum.
11. Set of printing inks according to any one of claims 6 to 10, wherein at least one printing ink comprises a reflecting pigment.
12. Method for marking an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good, comprising the step of providing on said article a marking which is applied by using at least one printing ink according to any one of claims 1 to 6 or a set of printing inks according to any one of claims 7 to 11 or by using at

least one coating composition comprising at least one printing ink according to any one of claims 1 to 6 or a set of printing inks according to any one of claims 7 to 11.

13. Method according to claim 12, wherein said at least one coating composition is selected from the group consisting of, pasty inks comprising intaglio inks, letterpress inks, and offset inks, from the group consisting of liquid inks comprising screen printing inks, helio-flexo inks, and gravure inks, from the group consisting of toners for electrostatic or electrophoretic printing, or from the group consisting of ink-jet inks comprising drop-on-demand ink-jet inks and continuous ink-jet inks.
14. Method of authenticating an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good, comprising the steps of:
 - a) measuring an absorbance, reflectance or transmittance spectrum of an article marked by the method according to any one of claims 12 or 13, in the UV and/or visible and/or IR wavelength domain of the electromagnetic spectrum;
 - b) comparing the spectrum measured under a) and/or information derived therefrom with a corresponding spectrum of an authentic item and/or information derived therefrom
15. Method according to claim 14, wherein said method is carried out by a machine, such as a currency acceptor, a ticket validator, or a hand-held authentication device.
16. Method according to claim 14 or 15, wherein in step a) said spectrum is measured as a vector of digital values representing the absorption and/or reflection and/or transmission of

said marking at a selected number of wavelengths or over a selected number of wavelength domains.

17. Method according to any one of claims 14 to 16, wherein step b) is carried out by deriving the statistically independent hyper-color coordinates of said marking from the vector of digital values measured in step a), and comparing at least one of said hyper-color coordinates with a corresponding reference value of an authentic item, and deriving an authenticity indicator from the comparison result using a pre-established decision criterion.
18. Method for authenticating an article according to one of claims 14 to 17, wherein said spectrum is measured using a combination of a broad-band emitting light source and a plurality of narrow-band sensitive photodetectors, or using a combination of a broad-band sensitive photodetector and a plurality of narrow-band emitting light sources, or using a combination of a broad-band emitting light source and a diffractive or dispersive spectrometer device, or using a combination of a plurality of narrow-band emitting light sources, such as LEDs, and a broad-band sensitive imaging device, such as a CCD- or CMOS- camera, yielding spectral or hyperspectral imaging information.
19. Method for authenticating an article according to one of the claims 14 to 18, wherein said statistically independent hyper-color coordinates are derived from the measured spectrum by the means of a mathematical Least-Squares algorithm.
20. Marking, comprising at least one printing ink according to any one of claims 1 to 6 and/or at least one set of printing inks according to any one of claims 7 to 11.

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21. Article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good, comprising at least one marking according to claim 20.
22. Use of a dye or pigment having at least one absorption maximum in the visible range of the electromagnetic spectrum which is substantially different from the absorption maxima of the base colors of the CIEXYZ system and/or having an absorption band in the visible range of the electromagnetic spectrum whose band width at half intensity is narrower than 2400 cm^{-1} , preferably narrower than 2000 cm^{-1} , and most preferably narrower than 1500 cm^{-1} , for marking and/or authenticating an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good.
23. Use of a printing ink according to any one of claims 1 to 6 for marking and/or authenticating an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good.
24. Use of a set of printing inks according to any one of claims 7 to 11 for marking and/or authenticating an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good.
25. Use of a marking according to claim 20 for authenticating an article, such as a banknote, a document, a ticket, a foil, a thread, a label, a card, or a commercial good.

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Summary:

The invention discloses a printing ink, comprising at least one dye or pigment having at least one absorption maximum in the visible range of the electromagnetic spectrum which is substantially different from the absorption maxima of the base colors of the CIEXYZ system and/or having an absorption band in the visible range of the electromagnetic spectrum whose band width at half intensity is narrower than 2400 cm^{-1} , preferably narrower than 2000 cm^{-1} , and most preferably narrower than 1500 cm^{-1} , as well as a set of printing inks comprising at least two such printing inks, as well as a method for marking and/or authenticating a security article using such printing inks or such sets of printing inks.

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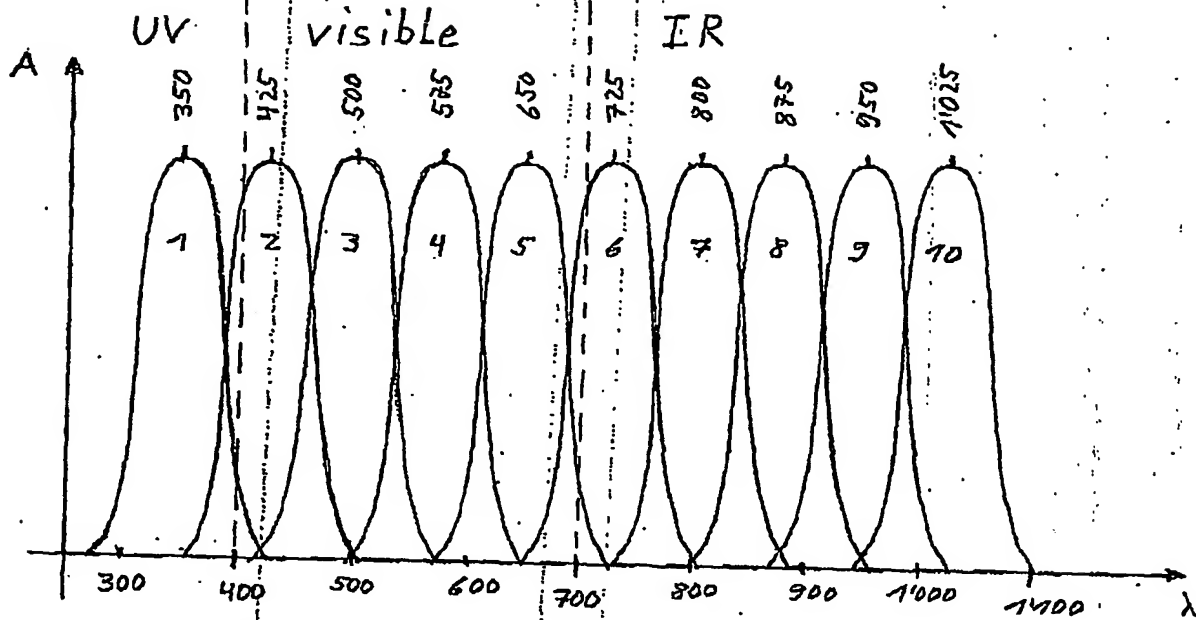
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Fig. 1:



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Fig. 2a

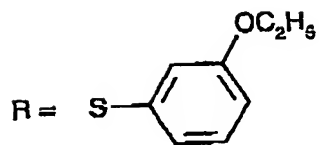
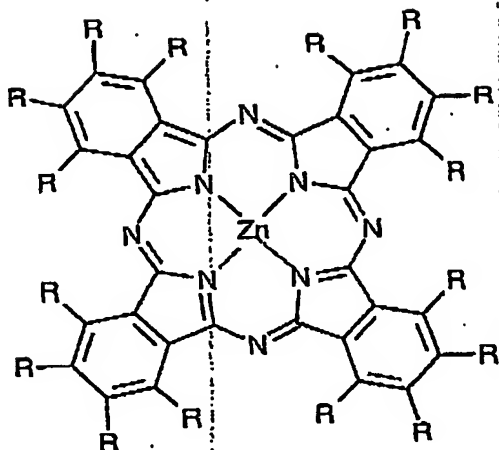
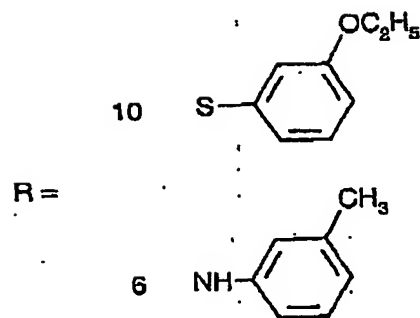
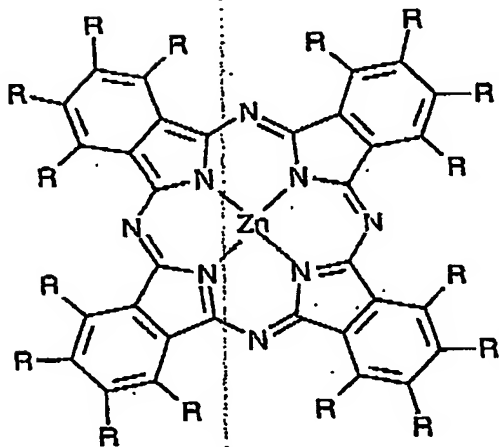


Fig. 2b

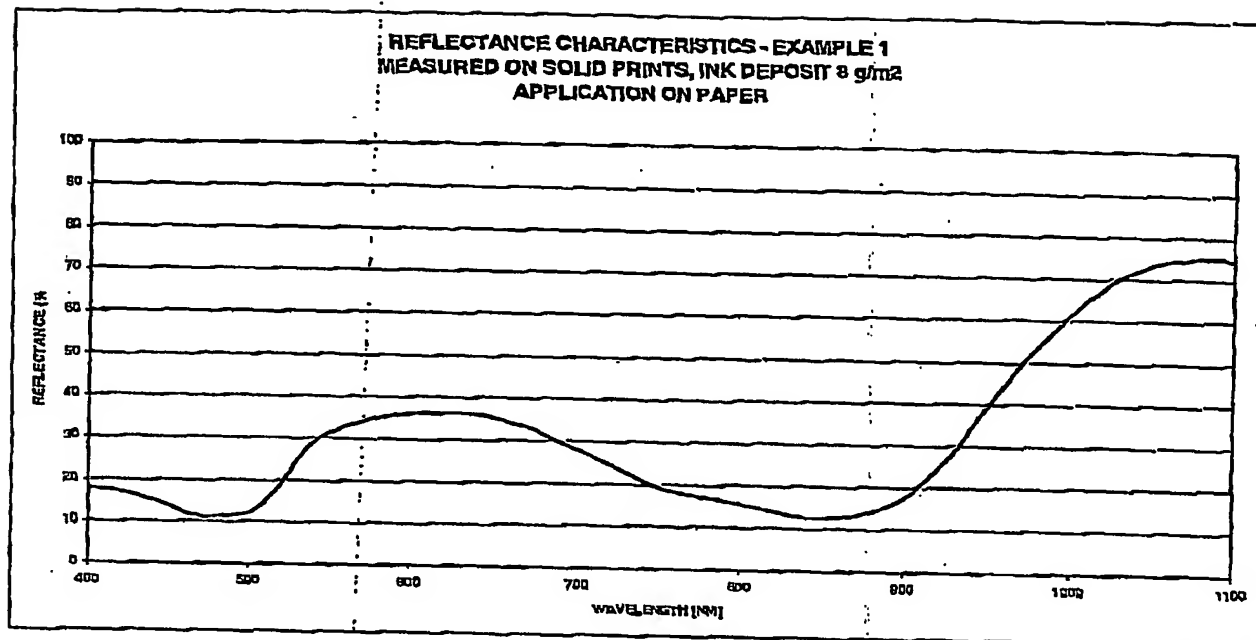


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Fig. 3



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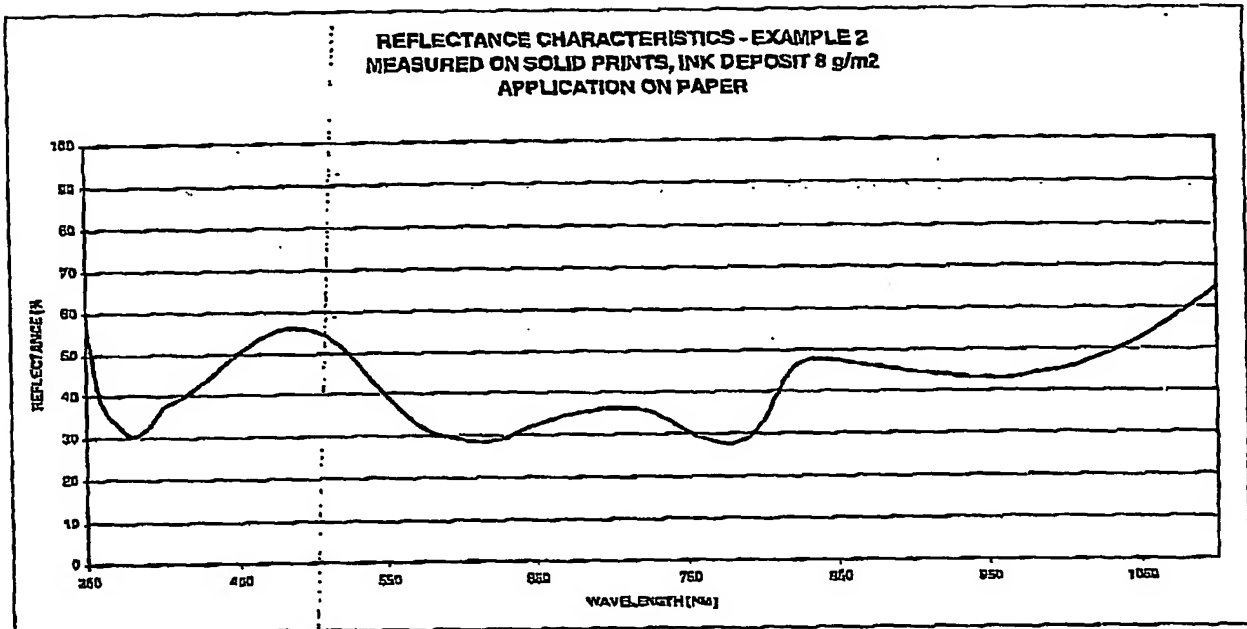
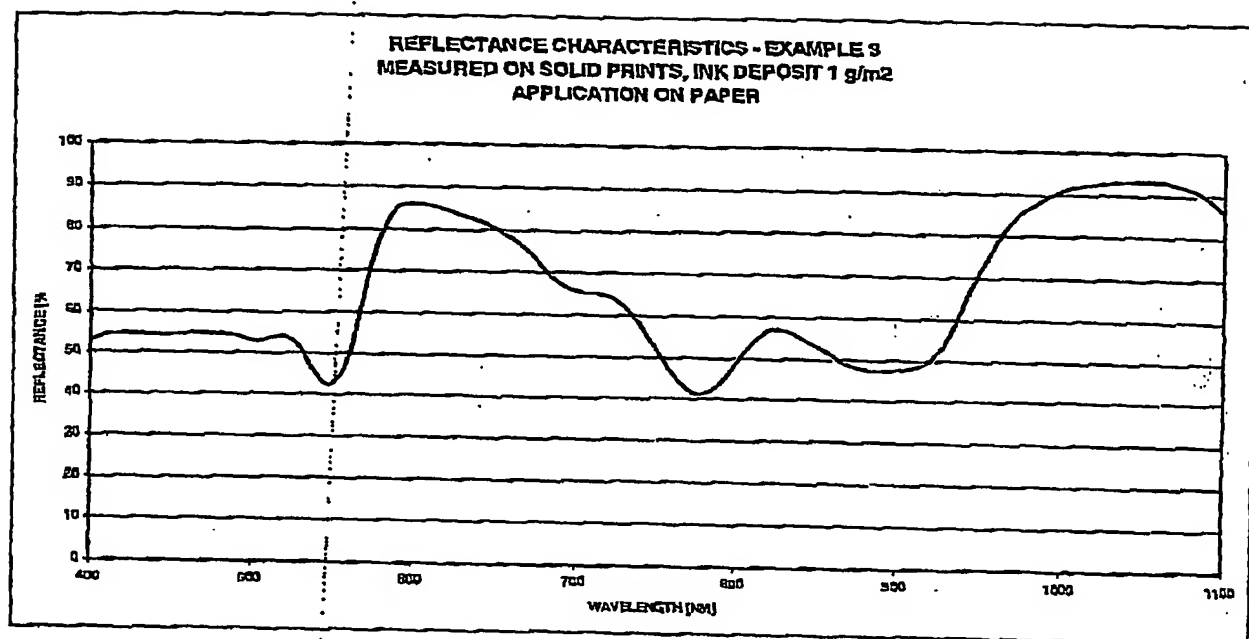
Fig. 4

Fig. 5

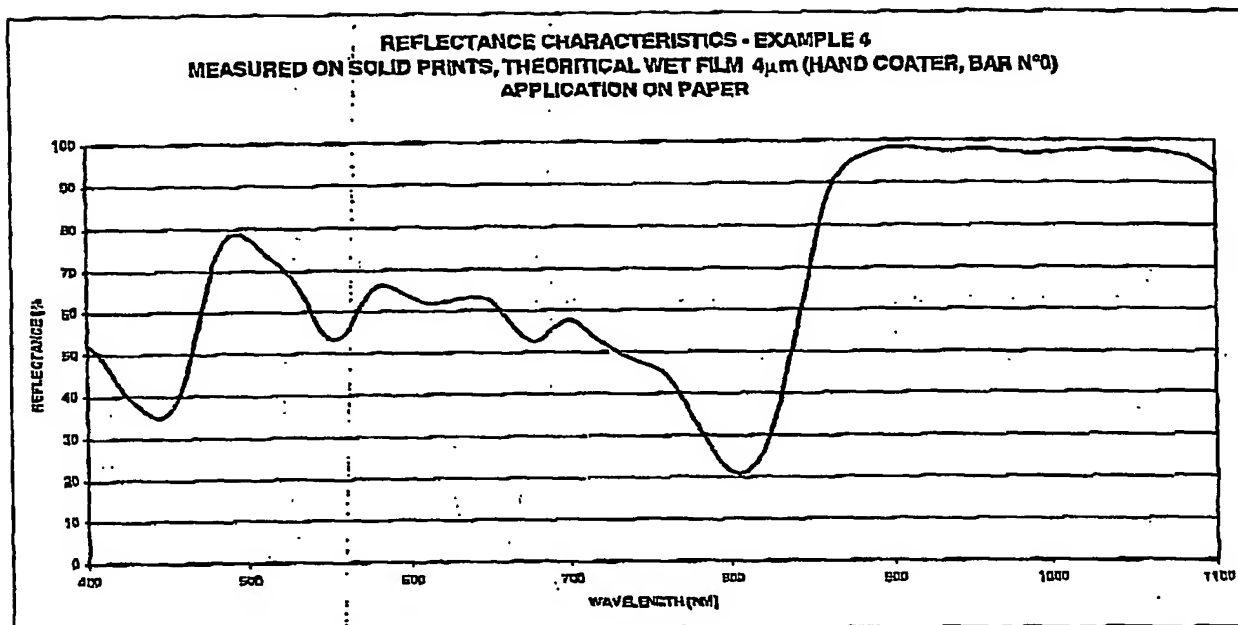


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Fig. 6



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Fig. 3

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REFLECTANCE CHARACTERISTICS - EXAMPLE 1
INK DEPOSIT 8 g/m²

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